

# Using the Lambert function in an exchange process with a time delay

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## Abstract

The current work describes the application of delay differential equations to the physical process of spin exchange, which affects the lineshape in pulsed nuclear magnetic resonance (NMR). The exchange process, usually described as instantaneous, is generalized by assuming non-negligible time for the exchange jump. Two approximate descriptions for the generalized system were proposed in a previous work. In one model the jump is assumed to occur via a transition state, which is treated in the standard equations as an ordinary state. In the other model, which is the focus of the present work, the jump is assumed to take place directly between the ordinary states, but with a time delay. The resulting delay differential equations for a two-site system are solved using the complex Lambert function. Some properties of the solution modes are studied in this work, in particular the possible occurrence of oscillations in the solutions.

## 1 Introduction

In pulsed NMR (nuclear magnetic resonance) experiments on a given system one measures a spectrum or "lineshape" which depends on the spin system

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being studied. The lineshape is affected in a characteristic manner by random processes in the system [1], in particular by chemical exchange processes [2]. The evolution of the spin system with chemical exchange is described by the Bloch-McConnell differential equations [3], in which it is assumed that each spin jumps instantaneously between two or more configurations. Using these equations one may calculate the observed lineshape under a variety of experimental settings.

We have recently studied a more general situation in which the time for the jump is not negligible [4]. Two models were suggested. In one model it is assumed that throughout the time of the jump the spin is found in a well defined transition state. Thus the system is described as having more states than the states considered ordinarily, but the jumps from a regular state to a transition state and vice versa are instantaneous. Therefore one may use ordinary differential equations, where the special character of the system is expressed in the set of parameters in the equations. In the other model the Lambert function is used to solve a set of differential equations with a time delay. The current work discusses stability and possibility of oscillations in the solutions, first in the standard description and then in the models with a time delay. Oscillations mean that the two site populations oscillate during the relaxation to equilibrium.

## 2 Standard model - stability and oscillations

One of the many versions of the NMR experiment is known as "saturation recovery", where for a two-site exchanging system the relevant equations needed for calculating the measured signal are the following ones [4]:

$$\frac{d}{dt} \begin{pmatrix} M_{zA}(t) \\ M_{zB}(t) \end{pmatrix} = \begin{pmatrix} -R_A - k_{A,B} & k_{B,A} \\ k_{A,B} & -R_B - k_{B,A} \end{pmatrix} \cdot \begin{pmatrix} M_{zA}(t) \\ M_{zB}(t) \end{pmatrix} + \begin{pmatrix} M_{0A} \cdot R_A \\ M_{0B} \cdot R_B \end{pmatrix} \quad (1)$$

where the notation  $R_X = \frac{1}{T_{1X}}$  is used for  $X = A, B$  ( $A, B$  are the two sites), and  $k_{X,Y}$  is the jump rate from site  $X$  to site  $Y$ .

This is a particular case of a general system with  $n$ -site spin exchange, which is [5]:

$$\frac{d}{dt} (\mathbf{x}(t)) = (\mathbf{P}) \cdot (\mathbf{x}(t)) + (\mathbf{b}) \quad (2)$$

with

$$P_{i,i} = -R_i - \sum_{\substack{j=N \\ j \neq i}} k_{i,j} \quad (3a)$$

$$P_{i,j} = k_{j,i} \quad (for \ i \neq j) \quad (3b)$$

In general the eigenvalues of a matrix are equal to those of its transpose, because  $\det(A - \lambda I) = \det(A - \lambda I)^t = \det(A^t - \lambda I)$ . For the  $\mathbf{P}$  matrix the eigenvalues of the transpose  $\mathbf{Q} = \mathbf{P}^t$  may be studied using the Gerschgorin circle theorem:

$$|\lambda - Q_{i,i}| \leq \sum_{\substack{j=N \\ j \neq i}} |Q_{i,j}| \quad (4)$$

This ensures stability of the corresponding equations, so the system described by Eq. (2) has stable solutions which decay with time to the equilibrium solution, given by the  $\mathbf{b}$  vector.

The occurrence of oscillations in the decaying solutions depends on the details of the system. In many exchanging systems the equilibrium populations of the different sites are equal. Combining this with the "microscopic reversibility" (or "mass balance") condition [4] the jump rates are symmetric:  $k_{j,i} = k_{i,j} \ \forall i, j$ . Then the matrix  $\mathbf{P}$  is real and symmetric, and therefore all its eigenvalues are real. Consequently, in a system where all jump rates are symmetric the solutions decay without any oscillations.

The question remains for the more general case, where the jump rates are not necessarily symmetric. For a 2-site system, the eigenvalues of the system of Eq. (1) are:

$$\begin{aligned} \lambda_{1,2} &= -\frac{1}{2} \cdot (R_A + R_B + k_{A,B} + k_{B,A}) \\ &\mp \frac{1}{2} \sqrt{(R_A + R_B + k_{A,B} + k_{B,A})^2 - 4 \cdot (R_A \cdot k_{B,A} + R_B \cdot k_{A,B} + R_A \cdot R_B)} \\ &= -\frac{1}{2} \cdot (R_A + R_B + k_{A,B} + k_{B,A}) \\ &\mp \frac{1}{2} \sqrt{((R_A - R_B) + (k_{A,B} - k_{B,A}))^2 + 4 \cdot k_{A,B} \cdot k_{B,A}} \end{aligned} \quad (5)$$

These eigenvalues lead to a pure decay of the solutions, without oscillations. For a similar 3-site system, if one assumes:  $R_A = R_B = R_C = R$  and

defines:

$$\sigma_1 = (2 \cdot R + k_{A,B} + k_{B,A} + k_{A,C} + k_{C,A} + k_{B,C} + k_{C,B}) \quad (6a)$$

$$\sigma_2 = k_{A,B} \cdot (k_{C,A} + k_{B,C} + k_{C,B}) + k_{B,A} \cdot (k_{C,A} + k_{A,C} + k_{C,B}) + k_{A,C} \cdot (k_{B,C} + k_{C,B}) + k_{B,C} \cdot k_{C,A} \quad (6b)$$

then the eigenvalues are:

$$\lambda_{1,2} = -\frac{1}{2}\sigma_1 \mp \frac{1}{2}\sqrt{(\sigma_1)^2 - 4 \cdot (\sigma_2 + R \cdot (\sigma_1 - R))} \quad (7a)$$

$$\lambda_3 = -R \quad (7b)$$

In this case, oscillations may occur, depending on the parameters.

### 3 Exchange with time delay - transition state model

The above description was based on the instantaneous jump assumption. We shall now generalize to the case of non-negligible jump time, and examine the implications for a two-site system. In that case the magnetization which leaves. e.g., site A at time  $t$  reduces immediately the magnetization at the site, but the magnetization which is added to site A due to the exchange must have left site B at an earlier time,  $t - \tau$  where  $\tau$  is the delay for the jump. We assume here a constant value (for all times) of the delay, equal for the two jump directions. Now one has to solve the two dimensional system of differential equations with a delay:

$$\begin{aligned} \frac{d}{dt} \begin{pmatrix} M_{zA}(t) \\ M_{zB}(t) \end{pmatrix} = & \begin{pmatrix} -R_A - k_{A,B} & 0 \\ 0 & -R_B - k_{B,A} \end{pmatrix} \cdot \begin{pmatrix} M_{zA}(t) \\ M_{zB}(t) \end{pmatrix} \\ + & \begin{pmatrix} 0 & k_{B,A} \\ k_{A,B} & 0 \end{pmatrix} \cdot \begin{pmatrix} M_{zA}(t - \tau) \\ M_{zB}(t - \tau) \end{pmatrix} + \begin{pmatrix} M_{0A} \cdot R_A \\ M_{0B} \cdot R_B \end{pmatrix} \end{aligned} \quad (8)$$

Two alternative models were proposed for such a system [4]. In one model it is assumed that during the non-negligible transition time the spin is in a definite state, characterized by its contribution to the magnetization. Then

the set of available states of the spin may be augmented from  $A, B$  to  $A, B, C$  where  $C$  is the transition state. Then one may use the standard exchange model, but for three sites, where one site (the transition site  $C$ ) serves as an intermediate between the other two sites. In this manner the equations are converted back to ordinary differential equations:

$$\frac{d}{dt}(\mathbf{x}(t)) = (\mathbf{A}) \cdot (\mathbf{x}(t)) + (\mathbf{b}) \quad (9)$$

With the following definitions:

$$(\mathbf{x}(t)) = \begin{pmatrix} M_{zA}(t) \\ M_{zB}(t) \\ M_{zC}(t) \end{pmatrix} \quad (10)$$

$$(\mathbf{A}) = \begin{pmatrix} -R_A - k_{A,C} & 0 & k_{C,A} \\ 0 & -R_B - k_{B,C} & k_{C,B} \\ k_{A,C} & k_{B,C} & -R_C - k_{C,A} - k_{C,B} \end{pmatrix} \quad (11)$$

The model assumes that exchange occurs only in two ways: either from site  $A$  or  $B$  to site  $C$ , or from site  $C$  to site  $A$  or  $B$ . Assuming mass balance:  $k_{A,C}M_{0A} = k_{B,C}M_{0B}$  and other simplifying assumptions [4] (including equality of all jump rates) the equation becomes:

$$\begin{aligned} \frac{d}{dt} \begin{pmatrix} M_{zA}(t) \\ M_{zB}(t) \\ M_{zC}(t) \end{pmatrix} &= \begin{pmatrix} -(R+k) & 0 & \frac{1}{\tau} \\ 0 & -(R+k) & \frac{1}{\tau} \\ k & k & -(R+\frac{2}{\tau}) \end{pmatrix} \cdot \begin{pmatrix} M_{zA}(t) \\ M_{zB}(t) \\ M_{zC}(t) \end{pmatrix} \\ &+ M_{0A} \cdot R \cdot \begin{pmatrix} 1 \\ 1 \\ \frac{k \cdot \tau}{2} \end{pmatrix} \end{aligned} \quad (12)$$

For exchange with delay, it is expected that  $k \cdot \tau \ll 1$ . The solution for Eq. (12) for each site is a superposition of three decaying non-oscillating exponentials (in addition to a constant term) with the eigenvalues:

$$\lambda_1 = -R \quad (13a)$$

$$\lambda_2 = -(R+k) \quad (13b)$$

$$\lambda_3 = -(R+k) - \frac{2}{\tau} \quad (13c)$$

The eigenvalues obtained in this simplified model are assumed to represent dominant eigenvalues of the exact system, while other components are supposed to be negligible. The validity of this approximation should be determined experimentally.

## 4 Exchange with time delay - direct solution

### 4.1 The method of solution

The second model to be examined relies on a direct solution of (7), which is re-arranged as [4]:

$$\frac{d}{dt}(\mathbf{x}(t)) + (\mathbf{A}) \cdot (\mathbf{x}(t - \tau)) + (\mathbf{B}) \cdot (\mathbf{x}(t)) = (\mathbf{u}) \quad (14)$$

with the definitions

$$(\mathbf{A}) = \begin{pmatrix} 0 & -k_{B,A} \\ -k_{A,B} & 0 \end{pmatrix} \quad (15)$$

$$(\mathbf{B}) = \begin{pmatrix} R_A + k_{A,B} & 0 \\ 0 & R_B + k_{B,A} \end{pmatrix} \quad (16)$$

The equation is assumed to apply only for  $t > 0$ , whereas for earlier time values a preshape function has to be assumed:

$$\mathbf{x}(t) = \phi(t) \quad \text{for} \quad 0 > t > -\tau \quad (17)$$

For simplicity it is assumed here that the exchange rates are symmetric:  $k_{B,A} = k_{A,B}$ . To solve the characteristic equation and consequently the original problem, it is proposed to use the Lambert function [6] which is defined by

$$W(h) \cdot e^{W(h)} = h \quad (18)$$

In general this is a complex function with an infinite number of branches  $W_p(h)$ . An expansion for the principal branch (with radius of convergence  $= \frac{1}{e}$ ) is [6]

$$W_0(s) = \sum_{n=1}^{\infty} \frac{(-n)^{n-1}}{n!} \cdot s^n \quad (19)$$

An asymptotic expansion for the other branches for very large  $s$ , or for  $s \rightarrow 0$  (and also for the principal branch for very large  $s$ ) is [6]

$$W_p(s) = \ln_p(s) - \ln(\ln_p(s)) + \sum_{l=0}^{\infty} \sum_{m=1}^{\infty} C_{lm} \frac{(\ln(\ln_p(s)))^m}{(\ln_p(s))^{l+m}} \quad (20)$$

with the definition:

$$\ln_p(s) = \ln(s) + 2\pi \cdot p \cdot i \quad (\text{integer } p) \quad (21)$$

( $i$  is the imaginary unit) and with the coefficients:

$$C_{lm} = \frac{1}{m!} \cdot (-1)^l \cdot \begin{bmatrix} l+m \\ l+1 \end{bmatrix} \quad (22)$$

defined in terms of the Stirling cycle numbers. Using Lambert's function it is shown that the characteristic matrix equation is solved by

$$s \cdot \mathbf{I} = \frac{1}{\tau} \cdot W(-\mathbf{A} \cdot \tau \cdot e^{\mathbf{B} \cdot \tau}) - \mathbf{B} \quad (23)$$

where Lambert's function for a matrix is defined using the definition of a matrix exponential [4]. The behavior of the three lowest branches  $W_p(x)$  for a small real argument  $x$  is shown in Fig. 1. Branch  $p = 0$  (the principal branch) is real if  $x > -\frac{1}{e}$ , branch  $p = -1$  is real if  $0 > x > -\frac{1}{e}$ , and branch  $p = 1$  (like all other branches) has complex values for any value of  $x$ .

For the case in which the matrices  $\mathbf{A}$ ,  $\mathbf{B}$  commute the solution for (13) is

$$x(t) = \sum_{m=-\infty}^{\infty} \xi_m(t) \cdot G_m + \sum_{m=-\infty}^{\infty} \xi_m(t) \cdot H_m \quad (24)$$

with the modes (time dependent matrices)

$$\xi_m(t) = \exp\{S_m \cdot t\} = \exp\left\{\left(\frac{1}{\tau} \cdot W_m(-\mathbf{A} \cdot \tau \cdot e^{\mathbf{B} \cdot \tau}) - \mathbf{B}\right) \cdot t\right\} \quad (25)$$

where the vectors  $G_m$  represent the solution for the homogeneous equation and the vectors  $H_m$  represent the particular solution for the inhomogeneous equation. Diagonalizing the matrix argument of the Lambert function one

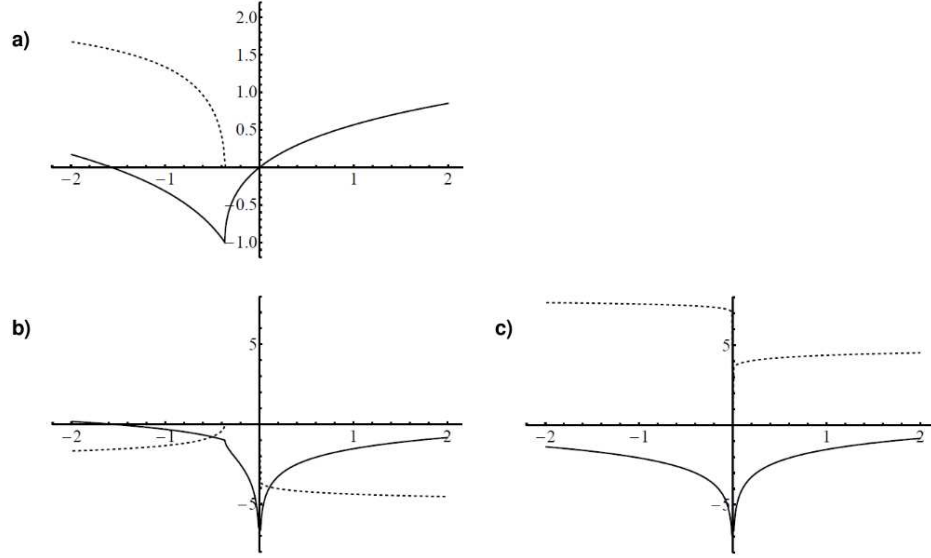


Figure 1: a)  $Re(W_0(x))$  (solid line) and  $Im(W_0(x))$  (dashed line), for real argument  $x$ . A singularity occurs for  $x = -\frac{1}{e}$ . b)  $Re(W_{-1}(x))$  (solid line) and  $Im(W_{-1}(x))$  (dashed line), for real argument  $x$ . A singularity occurs for  $x = -\frac{1}{e}$  and also for  $x = 0$ . c)  $Re(W_1(x))$  (solid line) and  $Im(W_1(x))$  (dashed line), for real argument  $x$ . A singularity occurs for  $x = 0$ .

may calculate its value on scalars [4], and the eigenvalues of  $S_m$  for the two-site problem are:

$$\lambda_1(m) = \frac{1}{\tau} \cdot W_m \left( -k \cdot \tau \cdot e^{(R+k) \cdot \tau} \right) - (R + k) \quad (26a)$$

$$\lambda_2(m) = \frac{1}{\tau} \cdot W_m \left( k \cdot \tau \cdot e^{(R+k) \cdot \tau} \right) - (R + k) \quad (26b)$$

The stability of the system is shown elsewhere [7]. An example of the actual values of these eigenvalues is shown in Fig. 2. For the range of parameters taken here, the eigenvalues  $\lambda_1(m)$  form pairs of complex conjugate



values except for the real eigenvalues  $\lambda_1(0)$  ,  $\lambda_1(-1)$  and the eigenvalues  $\lambda_2(m)$  form pairs of complex conjugate values except for the real eigenvalue  $\lambda_2(0)$  [7] .

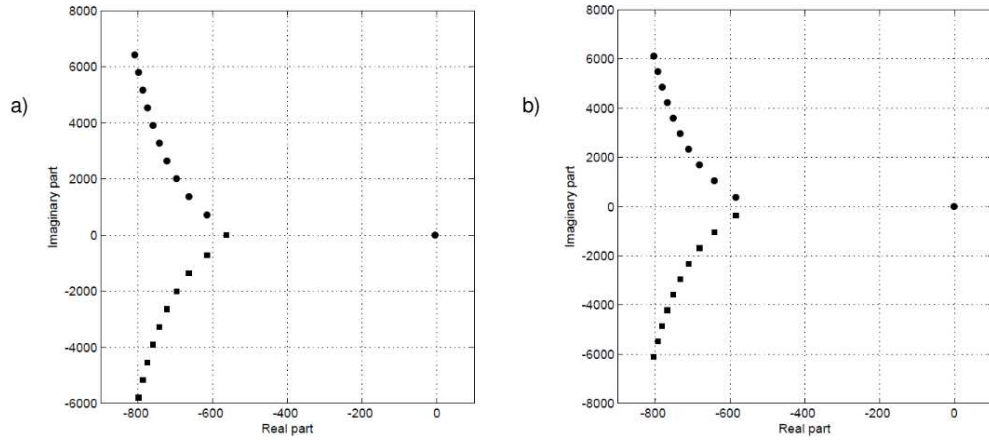


Figure 2: a) The eigenvalues  $\lambda_1(m)$  for branches:  $-10 \leq m \leq 10$  (circles:  $0 \leq m \leq 10$  , squares:  $m < 0$ ), for the parameters:  $R = 1$ ,  $k = 2$  and  $\tau = 0.01$  (intermediate exchange rate). The magnitude of both real and imaginary parts increases monotonically with the absolute value of the branch number. b) The eigenvalues  $\lambda_2(m)$  for branches:  $-10 \leq m \leq 10$  (circles:  $0 \leq m \leq 10$  , squares:  $m < 0$ ), for the same parameters. The magnitude of both real and imaginary parts increases monotonically with the absolute value of the branch number.

Now the possibility of oscillations will be addressed for the solutions based on the Lambert function. Obviously, the infinite number of pairs of complex conjugate eigenvalues result in an infinite number of oscillating components in the solution. This is completely different from the model without delay, and from the "transition state" model for the case with delay, where there was

a limited number of components, all of them non-oscillating (for the two-site case). There are, however, two questions with respect to the oscillations in the Lambert function model. First, what are the non-oscillating components, and what are the conditions for their appearance in the solution, and second, what is the relative importance of the oscillating components in the solution. The second question is easy to answer for the relevant range of parameters from Fig. 2 (see more detailed discussion in [7] ). The complex eigenvalues have a large negative real part, which means fast decay, and also a large imaginary part, which means fast oscillations, that may effectively cause an averaging over its values, so these components have only a minor effect on the solution.

Several facts result from the expressions for the eigenvalues given above, and from the expansions of the Lambert function shown above. First, non-oscillatory terms in the solution may only come from branch 0 and branch -1. Second,  $\lambda_2(0)$  is always real, and  $\lambda_2(-1)$  is always complex. As for  $\lambda_1(0)$  and  $\lambda_1(-1)$ , both of them are real if

$$k \cdot \tau \cdot e^{(R+k) \cdot \tau} < \frac{1}{e} \quad (27)$$

and both of them are complex otherwise (the point  $\frac{1}{e}$  itself is a singularity). Thus, using the definitions:  $x = k \cdot \tau$  and  $r = R \cdot \tau$  the requirement for non-oscillatory terms with  $\lambda_1(0)$  and  $\lambda_1(-1)$  is:

$$x \cdot e^x < e^{-r-1} \quad (28)$$

or

$$\ln(x) + x < -r - 1 \quad (29)$$

thus the relative values of  $R$  and  $k$  (and consequently of  $r$  and  $x$ ) determine the appearance of oscillations in these components. Fig. 3.a) shows the function:  $\ln(x) + x$  compared with:  $-r - 1$  for three arbitrary values of  $r$  over a certain range of  $x$  values. In this case,  $r = 10$  leads to oscillations whereas  $r = 0.1$  and  $r = 1$  do not do so. In Figs. 3.b)- 3.d) a similar comparison is made for several sets of parameters, corresponding to several possible physical situations.

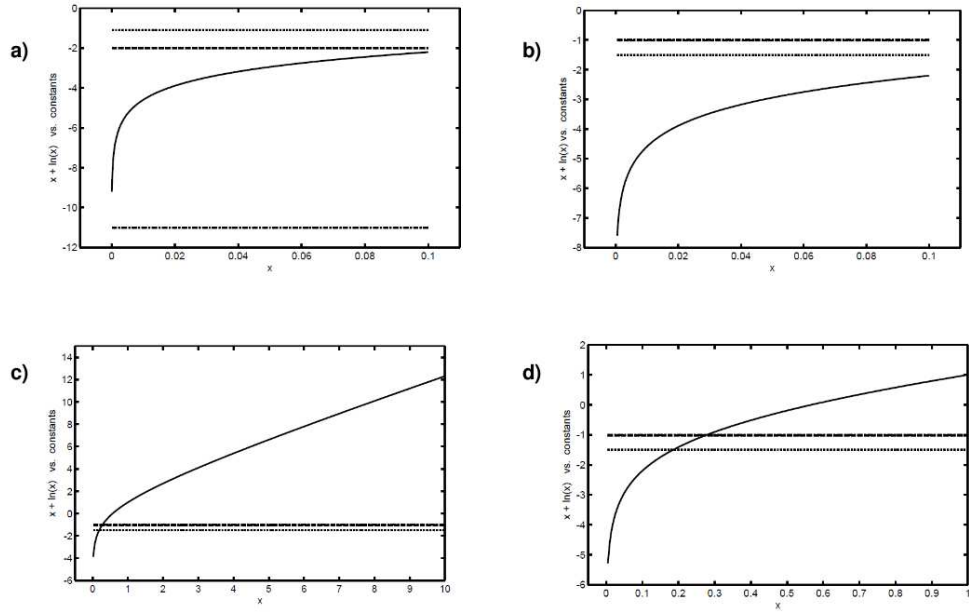


Figure 3:  $x + \ln(x)$  (solid line) as a function of  $x = k \cdot \tau$  compared with  $-r - 1$  ( $r = R \cdot \tau$ ) for the following cases: a)  $r = 0.1$  (dotted line),  $r = 1$  (dashed line),  $r = 10$  (dot-dashed line). b) - d):  $r = 0.002$  (dot-dashed line, corresponds to slow exchange),  $r = 0.02$  (dashed line, corresponds to fast or intermediate exchange),  $r = 0.5$  (dotted line, corresponds to fast exchange with a long delay), for: b) range of small  $x$ , c) wide range of  $x$ , d) region of onset of oscillations: intersections at  $(r, x) = (0.002, 0.278)$ ,  $(0.02, 0.274)$ ,  $(0.5, 0.185)$ .

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